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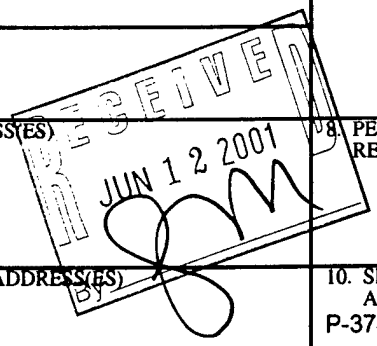

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13. ABSTRACT (Maximum 200 words)

This research explored a variety of interrelated topics in the general area of controlling molecular dynamics phenomena with tailored laser pulses. The research concerned the development of new algorithms for the design of such laser pulses, as well as for directly aiding the laboratory implementation of laser-controlled molecular processes. In addition, studies were carried out to explore the possibility of using data from control experiments to provide detailed insights into molecular properties. The theoretical research summarized in this report is having a direct impact on the rapidly emerging successful experiments in controlling molecular-scale processes.

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I. STATEMENT OF PROBLEM STUDIED.

Interest in the control of quantum systems has grown since the original suggestion, in the 1960's, of using lasers to manipulate chemical reactivity. This latter goal still stands as an important challenge, and there are very promising recent experimental results. Many more objectives are now of interest, including the manipulation of electron transport in semiconductors, excitons in solids, quantum optics, quantum computers, and high harmonic generation, amongst others. In addition, there is the prospect of using similar quantum system control techniques to invert the observed dynamics data and learn high quality information about the underlying atomic-scale interactions. The primary means of control in all of these areas is through the use of tailored laser fields, whose formation is an emerging laboratory technology exhibiting considerable flexibility for practical applications.

Regardless of the application, the essence of the underlying control concept is captured by the goal

$$|\psi_i\rangle \rightarrow |\psi_f\rangle \tag{1}$$

of steering a quantum system from a specified initial state $|\psi_i\rangle$ to a desired final state $|\psi_f\rangle$. In the laboratory, the actual objective is an expectation value $\langle\psi_i|O|\psi_f\rangle$ over a suitable observable operator *O*. These statements may also be generalized to include the density matrix, rather than the wavefunction. As a problem in quantum system control, these goals are typically expressed in terms of seeking a tailored laser electric field ε(t) that couples into the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = [H_0 - \mu\cdot\varepsilon(t)]|\psi\rangle \tag{2}$$

through the dipole m. By assumption, the dynamics under the free Hamiltonian H_0 does not evolve the system in the desired way expressed in Eq. (1). Regardless of the physical application, the general mechanism for achieving quantum control is through the manipulation of constructive and destructive quantum wave interferences. The goal is to create maximum constructive interference in the state $|\psi_f\rangle$ according to Eq. (1), while simultaneously achieving maximum destructive interference in all other states $|\psi_{f'}\rangle$, $f' \neq f$ at the desired target time T. A simple analogy to this process is the traditional double slit experiment. However, a wave interference experiment with two slits will lead to only minimal resolution; in the context of quantum control, two pathways can produce limited selectivity when there are many accessible final states for discrimination. Thus, a multitude of effective slits needs to be created at the molecular scale in order to realize high quality control into a single state, while eliminating the flux into all other states, as best as possible. This logic leads to the need for introducing a control field ε(t) having sufficiently rich structure to simultaneously manipulate the phases and amplitudes of all of the pathways connecting the initial and final states.

The physical picture above prescribes a general mechanism for successful quantum control of any type: High quality control calls for the external field to fully cooperate with all of the dynamical capabilities of the quantum system. As quantum systems are generally capable of complex dynamical behavior, a simple conclusion is that the most successful control fields, in turn, will reflect that complex structure. This conclusion is borne out in the recent successful control experiments, especially those involving strong fields encompassing nonlinear quantum dynamical responses to the fields.

Recognizing that the general means of achieving control is through tailored optical fields $\varepsilon(t)$ lays the groundwork for the task of identifying successful control fields. This task may be accomplished either by computational design or direct discovery of the control field in the laboratory. The state of these two approaches has evolved considerably in recent years. It is natural to express control as an optimization process, as we always desire to produce the *best* outcome in the laboratory. The search for an optimal control field $\varepsilon(t)$ poses a nonlinear problem, in terms of either field design or a direct laboratory search for the field. The nonlinearity of the problem is important to appreciate, as it underlies the techniques and concepts being developed to determine the optimal fields. The origin of the nonlinearity lies in the control field $\varepsilon(t)$ being dependent on the current state $|\psi(t)\rangle$ of the evolving quantum system, as well as the future desired state $|\psi_f(T)\rangle$ or the physical objective. The relationship between the control field and the evolving state of the system can be highly complex in many cases. Nonlinearity is inherent in all areas of temporal system control, but it is an unusual perspective in quantum mechanics, which is normally thought of as involving linear dynamics: given the Hamiltonian, solve the linear Schrödinger equation. However, in the present context of quantum system control, we are seeking to find a piece of the Hamiltonian (i.e., $\varepsilon(t)$ in the term $-\mu\cdot\varepsilon(t)$), which is initially unknown by definition of the physical control problem.

The research carried out under this grant explored quantum control from a variety of perspectives. A summary of these activities is given below.

II. SUMMARY OF THE MOST IMPORTANT RESULTS.

(1) SELECTIVE BOND DISSOCIATION AND REARRANGEMENT WITH OPTIMALLY TAILORED, STRONG-FIELD LASER PULSES [1].

This research used strong laser pulses that were tailored with closed-looped optimal control to govern specified chemical dissociation and reactivity channels in a series of organic molecules. Selective cleavage and rearrangement of chemical bonds having dissociation energies up to approximately 100 kilocalories per mole (about 4 electron volts) were reported for polyatomic molecules, including $(CH_3)_2CO$ (acetone), CH_3COCF_3 (trifluoroacetone), and $C_6H_5COCH_3$ (acetophenone). Control over the formation of CH_3CO from $(CH_3)_2CO$, CF_3 (or CH_3) from CH_3COCF, and $C_6H_5CH_3$ (toluene) from $C_6H_5COCH_3$ was observed with high selectivity. Strong-field control appeared to have generic applicability for manipulating molecular reactivity because the tailored intense laser fields (about 10^{13} watts per square centimeter) can dynamically Stark shift many

excited states into resonance, and consequently, the method has not been confined by resonant spectral restrictions found in the perturbative (weak-field) regime.

(2) NON-ITERATIVE OPTIMAL DESIGN OF QUANTUM CONTROLS [2].

A non-iterative means for quantum control design was introduced with the aim of offering practical designs that can later be fine-tuned with laboratory closed-loop techniques. The procedure recognized that Hamiltonians for realistic system control applications were rarely known accurately. The algorithm took advantage of this fact by allowing for managed deviations in the equations of motion, thus removing the standard Lagrange multiplier. Suitable time-dependent cost functional weights were introduced that eliminated the traditional final time matching condition, thereby producing non-iterative design equations as an initial value problem. Removal of the final time condition also eliminated the demand that the target state be reached at any artificially imposed time. Tests on a simple molecular system indicated that the algorithm led to well-behaved designs and that the weight functions were adequately estimated by order of magnitude analysis.

(3) ACHIEVING THE LABORATORY CONTROL OF QUANTUM DYNAMICS PHENOMENA USING NONLINEAR FUNCTIONAL MAPS [3].

This research introduced a new algorithm for achieving close-looped laboratory control of quantum dynamics phenomena. The procedure made use of nonlinear functional maps to exploit laboratory control data for revealing the relationship between control fields and their effect on the observables of interest. Control was achieved by (1) constructing maps by performing laboratory experiments during an initial learning phase, and then (2) searching the maps for fields that drive the system to the desired target during a separate, offline optimization stage. Once the map was learned, additional laboratory experiments were not necessarily required if the control target was changed. Maps also helped to determine the control mechanism and assess the robustness of the outcome to fluctuations in the field since they explicitly measured the nonlinear response of the observable to field variations. To demonstrate the operation of the proposed map-based control algorithm, two illustrations involving simulated population transfer were performed.

(4) OPTIMAL CONTROL OF CATALYTIC METHANOL CONVERSION TO FORMALDEHYDE[4].

An optimal control methodology was applied to find the head and oxygen flux profiles, distributed along the length of a plug flow reactor, for the conversion of methanol to formaldehyde. The calculations used models for the gas-phase and catalytic $[MoO_3 - Fe_2(MoO_4)_3]$ reactions. The reactor designs showed that a distributed heat flux improved formaldehyde yields, but an oxygen flux did not affect the results. Formaldehyde mass fractions of over 90% were achieved in the simulations. The solutions obtained, although not proven to be globally optimal, were of very high quality. A fully nonlinear robustness analysis of the formaldehyde production with respect to the catalyst model variables was performed by the use of a high dimensional model representation. This

representation was similar to the ANOVA decomposition used in statistics but did not require an increase in the number of data points as the dimensionality of the variable space increased. The most important variables were the catalyst surface area, and the rate of formaldehyde desorption. The yield improvement from employing optimized fluxes was found to be robust to the catalytic model parameter values.

(5) EXPLICIT GENERATION OF UNITARY TRANSFORMATIONS IN A SINGLE ATOM OR MOLECULE [5].

A constructive procedure for generating a prescribed unitary transform via the optically driven evolution of a multilevel atom was described. Assuming a clean separation of the coupled levels, the procedure employed the rotating wave approximation together with a decomposition of a unitary matrix into simpler matrix factors with specified structure. Applications to state preparation and observation were also provided.

(6) OPTIMAL CONTROL OF MOLECULAR MOTION: DESIGN, IMPLEMENTATION, AND INVERSION [6].

This work reviewed theoretical and experimental developments aimed at controlling molecular motion using tailored laser fields. Emphasis was given to seeking optimal designs for the laser controls and optimal implementation of the controls in the laboratory. Optimization on both counts provided a rigorous, flexible, and physically attractive means for obtaining the best possible control over molecular motion under and specified conditions. The theoretical design and laboratory implementation of control were best effected by a closed-loop process that drew on observations of the evolving molecular sample to steer it toward the desired target. Going beyond control, similar closed-loop laboratory learning concepts may lead to automated molecular monitors for inversion to systematically identify details of molecular Hamiltonians.

(7) MULTIDIMENSIONAL POTENTIAL SURFACES FROM THE DIRECT INVERSION OF PROBABILTIY DENSITY AND ENERGY SPECTRAL DATA [7].

This work presented a direct potential surface inversion algorithm for multidimensional quantum systems based on combining probability density and energy spectral data. The algorithm expressed the potential explicitly in terms of the eigenstate probability density and the associated eigenenergies. Simulations showed that the inversion could produce excellent results in the regular domain away from the asymptotic unidentifiable regions. The regular invertible domain of the potential could be adjusted by utilizing suitable spectral data. The inversion algorithm was successfully simulated to extract the potential surfaces of several one- and two-dimensional model systems.

(8) ALGORITHMS FOR CLOSED LOOP CONTROL OF QUANTUM DYNAMICS [8].

Most quantum systems considered for control by external fields are plagued by a serious lack of complete information about the underlying Hamiltonian. Traditional feedback control techniques are generally not appropriate due to the latter problem, as well as the ultrafast nature of typical quantum dynamics phenomena and the fact that observations of the quantum system will inevitably lead to a disturbance which may often by contradictory to the desired control. In contrast, learning control techniques have a special role to play in the manipulation of quantum dynamics phenomena. The unique capabilities of quantum systems making them amenable to learning control are (a) the ability to have very large numbers of identical systems for submission to control, (b) the high duty cycle of laboratory laser controls, and (c) the ability to observe the impact of trial controls at ultrafast time scales. Various learning algorithms were proposed in this work to guide this control process. The present work discussed these proposals, as well as some new perspectives.

(9) COMPENSATING FOR SPATIAL LASER PROFILE EFFECTS ON THE CONTROL OF QUANTUM SYSTEMS [9].

This research investigated the influence of experimentally nonuniform spatial laser profiles on controlling quantum dynamics. The influence of Gaussian (TEM_{00}), donut (TEM^{*}_{01}), and uniform laser profiles upon quantum control yield was considered. Nonuniform laser profiles can reduce the control yield, but it was shown that this effect could be diminished, by designing optimized laser pulses explicitly taking into account the spatial laser profile. These laser pulses were of significantly different structure than the ones for uniform profiles. This result suggested that an analysis of experimental laser fields to gain information on the resultant physical processes would be more difficult for pulses with nonuniform profiles. The simulations indicated that direct closed loop control in the laboratory could learn to operate effectively with nonuniform profiles.

(10) QUANTUM CONTROL BY DECOPMOSITIONS OF SU(2) [10].

Constructive procedures that make no use of optimization or iterative calculations for the control of many quantum and classical systems, via controls that are required to satisfy

constraints on their power of pulse area, were presented. These procedures were based on structured decompositions of SU(2). A general technique for obtaining such structures decompositions was given. Illustrative examples were provided.

(11) INCORPORATING PHYSICAL IMPLEMENTATION CONCERNS INTO CLOSED LOOP QUANTUM CONTROL EXPERIMENTS [11].

In quantum control experiments, it is desirable to build features into the field that address physical concerns such as simplicity, robustness, dynamical coherence, power expenditure, etc. With a judicious choice for the cost functional, it was possible to incorporate such secondary features into the field, often without altering the experimental procedure of apparatus. Through simulated closed-loop population transfer experiments, this research demonstrated the benefit of carefully designed cost functionals. As specific examples, it addressed two common physical concerns: removing extraneous structure from the control pulse and finding robust fields. Removing unnecessary field components was critical if information about the mechanism was to be interpreted from the structure of the optimal pulse. Robust fields produced a stable outcome despite noise in the field and, perhaps, environmental inhomogeneities in the quantum system as is typical of condensed phase experiments.

(12) EXTRACTING MOLECULAR HAMILTONIAN STRUCTURE FROM TIME-DEPENDENT FLUORESCENCE INTENSITY DATA [12].

This research proposed a formalism for extracting molecular Hamiltonian structure from inversion of time-dependent fluorescence intensity data. The proposed method required a minimum of *a priori* knowledge about the system and allowed for extracting a complete set of information about the Hamiltonian for a pair of molecular electronic surfaces.

(13) WHITHER THE FUTURE OF CONTROLLING QUANTUM PHENOMENA? [13].

This review put into perspective the present state and prospects for controlling quantum phenomena in atoms and molecules. The topic considered including the nature of physical and chemical control objectives, the development of possible quantum control rules of thumb, the theoretical design of controls and their laboratory realization, quantum learning and feedback control in the laboratory, bulk media influences, and the ability to utilize coherent quantum manipulation as a means for extracting microscopic information. A *preview* of the field was presented, which suggested that important advances in the control of molecules and the capability of learning about molecular interactions may be reached through the application of emerging theoretical concepts and laboratory technologies.

(14) DRIVING WAVE PACKET RECURRENCES WITH OPTIMALLY MODULATED LASER PULSES [14].

In the weak-field limit, laser pulses optimized to induce vibrational wave packet recurrences in excited state potentials were calculated for Morse oscillators and for a real system [the $X^1\Sigma^+$ and $A^3\Pi(1)$ states of IBr]. The performance of the optimized pulses

was studied via simulated wave packet propagation. Such optimal light fields may be computationally generated given only the form of the electronic potential surfaces, knowledge of the particular ground state supplying population, and simple molecular constants. Thus it should be possible to use the modulation of light fields *experimentally* optimized to achieve recurrences in order to obtain substantial information regarding previously uncharacterized potential surfaces in both diatomic and polyatomic molecules. Moreover, it should be possible to generalize this approach to the strong-field limit.

(15) OPTIMAL CONTROL OF MOLECULAR MOTION EXPRESSED THROUGH QUANTUM FLUID DYNAMICS [15].

A quantum fluid dynamic (QFD) control formulation was presented for optimally manipulating atomic and molecular systems. In QFD, the control quantum system was expressed in terms of the probability density ρ and the quantum current j. This choice of variables was motivated by the generally expected slowly varying spatial-temporal dependence of the fluid-dynamical variables. The QDF approach was illustrated for manipulation of the ground electronic state dynamics of HCl induced by an external electric field.

(16) ASSESSING OPTIMALITY AND ROBUSTNESS FOR THE CONTROL OF DYNAMICAL SYSTEMS [16].

This work presented a general framework for assessing the quality and robustness of control over a deterministic system described by a state vector $\mathbf{x}(t)$ under external manipulation via control vector $\mathbf{u}(t)$. The control process was expressed in terms of a cost functional, including the physical objective, penalties, and constraints. The notions of optimality and robustness were expressed in terms of the sign and the magnitude of the cost functional curvature with respect to the controls. Both issues may be assessed from the eigenvalues of the stability operator S whose kernel $\mathbf{K}(t,\tau)$ was determined by $\overline{\delta u(t)}/\overline{\delta u(\tau)}$ for $t_0 < t$, $\tau \leq t_f$, where t_0 and t_f are the initial and final times of the control interval. The overbar denoted the constraint that the control satisfied the optimization conditions from minimizing the cost functional. The eigenvalues σ of S satisfying $\sigma < 1$ assured local optimality of a control solution, with $\sigma = 1$ being the critical value separating optimal solutions from false solutions (i.e., those with negative second variational curvature of the cost functional). In turn, the maximally robust control solutions with the least sensitivity to field errors also corresponded to $\sigma = 1$. Thus, sufficiently high sensitivity of the field at one time t to the field at another time τ (i.e., $\sigma > 1$) led to a loss of local optimality. A simple illustrative example was given from a linear dynamical system, and a bound for the eigenvalue spectrum of the stability operator was presented. The bound was employed to qualitatively analyze control optimality and robustness behavior. A second example of a nonlinear quartic anharmonic oscillator was also presented for stability and robustness analysis. In this case, it was proved that the control system kernel is negative definite, implying full stability but only marginal robustness.

(17) POTENTIAL SURFACES FROM THE INVERSION OF TIME DEPENDENT PROBABILITY DENSTIY DATA [17].

This research presented an algorithm that assessed the feasibility of inverting probability density data to extract potential surfaces. Such data admitted the generation of a noniterative quantum inversion algorithm that does not require the solution of the Schrödinger equation. Tikhonov regularization was employed to manage the singular nature of the problem. The inversion in regular regions had excellent accuracy, and an error analysis also indicated that the potential in the regular regions was stable under perturbations from noisy data. The regular regions of the potential were identified by the algorithm. The algorithm did not require knowledge of the excitation process initiating the evolution of the system. Analysis indicated that the most detailed potential surface information would result from broadband excitation leaving the molecule with significant population in as many quantum states as possible. The inversion algorithm was tested in a simulation for the O-H potential, which showed that the algorithm is very fast and reliable.

(18) NUCLEATION IN PERIODICALLY DRIVEN ELECTROCHEMICAL SYSTEMS [18].

This research calculated both the exponent and the prefactor in the nucleation rate of a periodically driven system. Nucleation dynamics was described by the Fokker-Planck equation for the probability distribution of the nuclei over their size. This distribution was found using the concept of the most probable (optimal) nucleation path. The results applied in a broad range of driving force amplitudes, from weak to moderately strong forces where the nucleation rate was changed exponentially strongly, and also in the broad range of the driving frequencies, from low-frequency driving, where the system followed the force adiabatically, to high-frequency nonadiabatic driving. For strong driving forces, the time dependence of the nucleation rate changed from strongly nonsinusoidal to a weak with the increasing frequency of driving. The response of the nucleation rate to the driving force was described in terms of logarithmic susceptibility (LS), which was obtained from the optimal nucleation path in the absence of the driving. LS is a smooth function of frequency, and therefore even a driving force with comparatively high frequency could change the modulation rate exponentially strongly. LS and the Faraday current were calculated for simple models of electrochemical systems, where the ac driving was produced by modulation of the electrode potential. The research also suggested how to find LS from measurements of the average nucleation rate.

(19) MONOTONICALLY CONVERGENT ALGORITHM FOR QUANTUM OPTIMAL CONTROL WITH DISSIPATION [19].

This work extended a monotonically convergent algorithm for quantum optimal control to treat systems with dissipation. The algorithm working with the density matrix was proved to exhibit quadratic and monotonic convergence. Several numerical tests were implemented in three-level model systems. The algorithm was exploited to control various targets, including the expectation value of a non-Hermitian operator, and off-diagonal elements of the density matrix.

(20) NONITERATIVE ALGORITHMS FOR FINDING QUANTUM OPTIMAL CONTROLS [20].

Iterative methods are generally necessary for solving the design equations to identify optimal quantum controls. Since iteration can be computationally intensive, it is significant to develop good approximate noniterative methods. This research presented noniterative techniques for achieving quantum optimal control over the expectation value of positive semidefinite operators. The noniterative methods were characterized by an order index. Zeroth-order methods involving no feedback from the objective were generally found to be inadequate. A proposed first-order noniterative algorithm was expected to often be a good approximation. Numerical tests verified the noniterative capabilities of the algorithm.

(21) MANAGING SINGULAR BEHAVIOR IN THE TRACKING CONTROL OF QUANTUM DYNAMICAL OBSERVABLES [21].

Singularities can arise in the external field obtained by tracking control of quantum mechanical systems. Whether or not the trajectory is disturbed by the presence of a singular point was shown to mainly depend on the average momentum along the trajectory at the moment of passing the singular point. If the singularity occurred on a turning point, the tracking will be quite unstable since the direction taken by the trajectory was very sensitive to field errors. The theoretical analysis of these situations yielded detailed conclusions about the impact of field singularities in quantum tracking control. A rank index was defined to characterize nontrivial singularities, and the rank was shown to play an important role in determining the tracking quality while passing over a singular turning point where the field has a unique solution. A special class of nontrivial singularities was identified by the ability to remove the singularity under a proper limiting process. These insights into the nature and influence of singularities in tracking control of quantum systems were beneficial for developing numerical schemes and for designing controls.

(22) A SELF-GUIDED ALGORITHM FOR LEARNING CONTROL OF QUANTUM-MECHANICAL SYSTEMS [22].

This work presented a general self-guided algorithm for direct laboratory learning of controls to manipulate quantum-mechanical systems. The primary focus was on an algorithm based on the learning of a linear laboratory input-output map from a sequence of controls, and their observed impact on the quantum-mechanical system. This map was then employed in an iterative fashion, to sequentially home in on the desired objective. The objective may be a target state at a final time, or a continuously weighted observational trajectory. The self-guided aspects of the algorithm were based on implementing a cost functional that only contains laboratory-accessible information. Through choice of the weights in this functional, the algorithm could automatically stay within the bounds of each local linear map and indicate when a new map is necessary for additional iterative improvement. Finally, these concepts could be generalized to include the possibility of employing nonlinear maps, as well as just the laboratory control instrument settings, rather

than observation of the control itself. An illustrative simulation of the concepts was presented for the control of a four-level quantum system.

(23) MOLECULAR DIPOLE FUNCTION INVERSION FROM TIME DEPENDENT PROBABILITY DENSITY AD ELECTRIC FIELD DATA [23].

A noniterative quantum mechanical algorithm was presented to extract the dipole function from time dependent probability density and external electric field data. The algorithm determined the dipole function as the solution of an exact linear integral equation without the need to solve the Schrödinger equation. The inversion in regular regions of the dipole was accurate and stable under perturbations from noisy data. The regular regions of the dipole were automatically identified by the algorithm, and Tikhonov regularization was employed. There was much freedom in the external electric field with the best choices generally producing broad excitations of many eigenstates. Field designs could be estimated from the Hamiltonian or through closed loop learning techniques in the laboratory. The inversion algorithm was tested in a simulation for O-H, which showed that the algorithm is very reliable. Since the inversion algorithm was fast, it was argued that closed loop laboratory learning techniques may be applied to optimally attain the dipole function in a desired region, whether local or as broad as possible, within the scope of the dynamics and control field capabilities.

(24) UNIFORM, RAPIDLY CONVERGENT ALGORITHM FOR QUANTUM OPTIMAL CONTROL OF OBJECTIVES WITH A POSITIVE SEMIDEFINITE HESSIAN MATRIX [24].

A uniform iteration method was presented for achieving quantum control over any real objective with a positive semidefinite Hessian matrix. Theoretical analysis showed that this uniform algorithm exhibited quadratic and monotonic convergence. Numerical calculations verified that for this uniform algorithm, within a few steps, the optimized objective functional came close to its converged limit. For some optimal control purposes, the objective itself was not required to be directly a physical observable, but it was only necessary that the objective have a suitable association with some desired physical observables. As an illustration of the algorithm, the control objective was chosen to achieve maximum population in a target state as well as minimum phase mismatch with the target state.

(25) CONTROL OF MICROWORLD CHEMICAL AND PHYSICAL PROCESSES [25].

An intense theoretical and laboratory effort is underway for controlling molecular motion with tailored laser pulses. Various means for designing laser pulses are available, but presently, the most viable procedure for achieving successful control over quantum systems in the laboratory is through the use of closed loop learning algorithms. The logic behind the operation of such algorithms was discussed.

(26) A RAPID MONOTONICALLY CONVERGENT ITERATION ALGORITHM FOR QUANTUM OPTIMAL CONTROL OVER THE EXPECTATION VALUE OF A POSITIVE DEFINITE OPERATOR [26].

A new iteration method was presented for achieving quantum optimal control over the expectation value of a positive definite operator. Theoretical analysis showed that this new algorithm exhibited quadratic and monotonic convergence. Numerical calculations verified that for this new algorithm, within a few steps, the optimized objective functional came close to its converged limit.

(27) ASSESSING OPTIMALITY AND ROBUSTNESS OF CONTROL OVER QUANTUM DYNAMICS [27].

This work presented a general framework for assessing the quality and robustness of control over quantum dynamics induced by an optic al field $\varepsilon(t)$. The control process was expressed in terms of a cost functional, including the physical objectives, penalties, and constraints. The first variations of such cost functional have traditionally been utilized to create designs for the controlling electric fields. Here, the second variation of the cost function was analyzed to explore (i) whether such solutions are locally optimal, and (ii) their degree of robustness. Both issues were assessed from the eigenvalues of the stability operator S whose kernel $K(t, \tau)$ was related to $\delta\varepsilon(t)/\delta\varepsilon(\tau)|_c$ for $0 < t, \tau \leq T$, where T was the target control time. Here, c denoted the constraint that the field satisfies the optimal control dynamical equations. The eigenvalues σ or S satisfying $\sigma < 1$ assured local optimality of the control solution, with $\sigma = 1$ being the critical value separating optimal solutions from false solutions (i.e., those with negative second variational curvature of the cost functional). In turn, the maximally robust control solutions with the least sensitivity to field errors also corresponded to $\sigma = 1$. Thus, sufficiently high sensitivity of the field at one time t to the field at another time τ (i.e., $\sigma > 1$) led to a loss of local optimality. An expression was obtained for a bound on the stability operator, and this result was employed to qualitatively analyze control behavior. From this bound, the inclusion of an auxiliary operator (i.e., other than the target operator) was shown to act as a stabilizer of the control process. It was also shown that robust solutions are expected to exist in both the strong- and weak-field regimes.

(28) ALGORITHMS FOR CLOSED LOOP ULTRAFAST CONTROL OF QUANTUM DYNAMICS [28].

Learning control techniques have a special role to play in the manipulation of quantum dynamics phenomena. The unique capabilities of quantum systems making them amenable to learning control are (a) the ability to have very large numbers of identical systems for submission to control, (b) the high duty cycle of laboratory laser controls, and (c) the ability to observe the impact of trial controls at ultrafast time scales. Various learning algorithms have been proposed to guide this control process. The present work discussed these proposals, as well as some new perspectives.

(29) CONTROLLING MOLECULAR MOTION: THE MOLECULE KNOWS BEST. [29].

Over the past decade, an intense effort has brought together theoretical and laboratory tools for controlling molecular motion with tailored laser pulses. Various means for designing laser pulses are available, including a new procedure, discussed here, for carrying out the effort when there is uncertainty in the Hamiltonian. Presently, the most viable general procedure for achieving successful control over quantum systems in the laboratory is through the use of closed loop learning algorithms. The logic behind the operation of such algorithms was discussed, along with a summary of several recent laboratory achievements exploiting closed loop learning to control quantum and nonlinear optical phenomena.

(30) AN ALGORITHM FOR OBTAINING POTENTIAL ENERGIES AND DIPOLE MOMENTS FOR A PAIR OF MOLECULAR ELECTRONIC SURFACES FROM INVERSION OF TIME-DEPENDENT FLUORESCENCE INTENSITY DATA [30].

This research proposed an algorithm for extracting potential energies and dipole moments for a pair of molecular electronic surfaces from the inversion of time-dependent fluorescence intensity data. The molecule was assumed to be initially in the ground vibrational state of the lower electronic surface and the wave packet was excited and guided by two locked external laser fields that drove transitions between the two electronic surfaces and between vibrational levels in each surface, respectively. This approach made possible simultaneous extraction of potentials and dipole moments for the two surfaces and of the electronic transition dipole moment. The use of time-dependent data facilitated a regularization procedure to stabilize the inversion and focus on the solution in the spatial region sampled by the wave packet.

(31) HIGH DIMENSIONAL MODEL REPRSENTATIONS GENERATED FROM LOW DIMENSIONAL DATA SAMPLES I: MP-CUT-HDMR [31].

High Dimensional Model Representation (HDMR) is a general set of quantitative model assessment and analysis tools for improving the efficiency of deducing high dimensional input-output system behavior. For a high dimensional system, an output $f(\mathbf{x})$ is commonly a function of many input variables $\mathbf{x} = \{x_1, x_2, ..., x_n\}$ with $n \sim 10^2$ or larger. HDMR described $f(x)$ by a finite hierarchical correlated function expansion in terms of the input variables. Various forms of HDMR can be constructed for different purposes. Cut- and RS-HDMR are two particular HDMR expansions. Since the correlated functions in an HDMR expansion are optimal, choices tailored to $f(\mathbf{x})$ over the entire domain of $\mathbf{x}$, the high order terms (usually larger than second order, or beyond pair cooperativity) in the expansion are often negligible. When the approximations given by the 1st and 2nd order Cut-HDMR correlated function were not adequate, this research presented a monomial based preconditioned HDMR method to represent the higher order terms of a Cut-HDMR expansion by expressions similar to the lower order ones with monomial multipliers. The accuracy of the Cut-HDMR expansion could be significantly improved using preconditioning with a minimal number of additional input-output samples without directly invoking the determination of higher order terms. The mathematical foundations of

monomial based preconditioned Cut-HDMR was presented, along with an illustration of its applicability to an atmospheric chemical kinetics model.

III. LIST OF ALL PUBLICATIONS SUPPORTED BY THIS GRANT AND BIBLIOGRPHY.

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IV. LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL AND DEGREES GRANTED.

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